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New Optical Materials for the Long-Wave (8-12 μm) Region:
Design Criteria for the Solid-State Chemist

by

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Submitted to Proc. Symp. Solid State Optical Materials,
Amer. Cer. Soc., Cincinnati, OH 29 Apr-3 May 1991,

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NEW OPTICAL MATERIALS FOR THE LONG-WAVE (8-12 μm) REGION: DESIGN CRITERIA FOR THE SOLID-STATE CHEMIST

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INTRODUCTION

Certain applications that utilize long-wavelength (8-12 μm) infrared (LWIR) windows require environmental durability and mechanical strength in addition to infrared optical transparency; i.e., *the window-materials must simultaneously serve as optical and structural ceramics*. The fundamental requirement of optical transparency in the long-wavelength region eliminates from consideration all well-known ceramic materials such as oxides, nitrides, and other light-anion compounds, making this a particularly difficult materials problem.

The structure-property relationships and chemical rationale used to guide both the screening of known compounds and the synthesis of new compounds likely to possess the desired properties rely on factors such as atomic mass, electronic configuration, coordination number, and crystal structure-type. The resulting criteria have directed our efforts in the synthesis and characterization of a number of ternary indium sulfide phases and calcium yttrium sulfide systems.

PROPERTY REQUIREMENTS AND CHEMICAL DESIGN

The requirement to serve as both an optical and structural ceramic dictates a certain set of chemical and physical properties for potentially useful compounds. These include (a) near-zero infrared absorption in the 8-12 μm region; (b) chemical inertness, i.e., water-, air-, and heat-stability; (c) melting points higher than 1000°C; (d) high mechanical strength; (e) low thermal expansion; and (f) a band gap greater than 2.0 eV. The comparison material currently available for application-purposes is ZnS. Diamond has an extremely promising set of properties, with the exception of air-stability at elevated temperatures, and is presently the subject of intense research and development efforts. The focus presented here is directed toward the less well-studied area of non-diamond alternatives to ZnS.

A guided chemical search for new materials requires, as a starting point, some attempt to correlate the pertinent properties with chemical and structural

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characteristics. The following observations are made, and correspond to the list of property-requirements given above:

- (a) *LWIR transparency* is determined by the masses of the constituent atoms and the nature of the chemical bonding among them. A simple "Hooke's Law" notion of the chemical bond (vibrational frequencies scale with $\sqrt{k/m}$, where k is the "spring constant" and m is mass) is surprisingly useful here. The relatively low fundamental vibrational frequencies required for 8-12 μm transparency are favored by weak chemical bonding (low k), heavy atoms (high m), and high coordination numbers (low k). The effect of mass can be dramatic; for example, comparison of the IR spectra of isostructural K_2SbPO_6 and K_2SbAsO_6 [1] indicates shifts of 200-300 cm^{-1} in the absorptions of the Group V-oxygen bonds.
- (b) *High chemical inertness* is favored by strong chemical bonds and three-dimensional crystal structures that promote resistance to hydrolysis, oxidation, and decomposition at temperatures many hundreds of degrees above ambient conditions.
- (c) *High melting point* is favored by the same factors as chemical inertness; i.e. strong bonding and three-dimensional structure-type.
- (d) *Mechanical strength*, including hardness and toughness, is also favored by strong chemical bonding in a three-dimensional crystal structure.
- (e) *Low thermal expansion* is favored by low cation coordination numbers and high formal oxidation states [2]; i.e., strong chemical bonding.
- (f) *High bandgap* (>2.0 eV) is favored by non-metallic bonding in insulating or semiconducting compounds. Ionic compounds should feature constituent "ions" with noble-gas or pseudo-noble-gas electronic configurations.

By considering the above trends, the "trade-off" situation is apparent: *The factors favoring a good LWIR optical ceramic conflict with those favoring a good structural ceramic.* Some type of compromise is therefore required.

Our compromise approach to this problem was developed by prioritizing the required properties. From practical considerations, LWIR transparency significantly superior to that of ZnS is by far the most important design-goal. Use of "anions" heavier than oxide, such as sulfide and/or phosphide, is therefore indicated. Cation coordination numbers must be higher than four in order to significantly improve transmission relative to that of ZnS [3-5]; thus, all crystal structure types based on tetrahedral coordination polyhedra are eliminated from consideration. On the other hand, cation coordination numbers as high as eight, while favoring good LWIR transparency [6], are likely to result in unacceptably

high coefficients of thermal expansion [2,6]. Cation coordination number six, featured in octahedrally based structural frameworks, is indicated as the compromise. The best target compounds will feature the heaviest cations that can adopt octahedral coordination by S²⁻ and/or P³⁻. To maintain bond strength, the cations should have high formal charges ($\geq 2^+$). For insulating or high-bandgap semiconducting behavior, "ionic" compounds featuring cations with closed shells are favored. Target crystal structures should be fully three-dimensional in their chemical bonding. These criteria taken together have guided our search for compounds likely to possess the desired optical transparency while still retaining acceptable (relative to ZnS) mechanical and chemical properties.

RESULTS AND DISCUSSION

Unequivocal measurements of intrinsic optical and mechanical properties are best made on high-quality single crystals; hence, our synthetic studies have included considerable efforts in the growth of single crystals of both reported and new compositions. Ultimate goals include the isolation of new, promising phases as well as confirmation/determination of structural details and their correlation with properties. The design-criteria described above have guided us to ternary indium-[7] and yttrium-based [3] sulfide systems that feature structural frameworks built of InS₆ or YS₆ octahedra. Eutectic halide flux-mixtures have led to successful crystal growth studies of a number of these complex sulfides, including some new phases [3,7]. Currently, quantitative infrared transmission measurements of single crystals using IR microscopy are underway and will be correlated with the results of ongoing structural determinations.

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